

# SHORT COMMUNICATION

## TRITERPENES FROM BALATA RESIN

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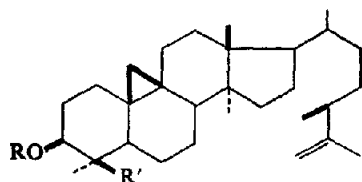
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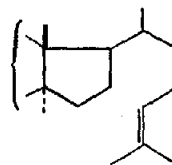
**Abstract**—Balata resin from the "balata tree" (*Mimusops globosa*) is shown to contain squalene,  $\beta$ -amyrin, lupeol, cycloartenol, 24-methylenecycloartenol and the ketones corresponding to the aforementioned alcohols.

THE LATEX which exudes from the balata tree (*Mimusops globosa*) (Sapotaceae) is used as a commercial source of *trans*-polyisoprene (gutta percha or balata hydrocarbon). The resinous constituents of crude balata may be extracted with acetone and it is these which constitute the balata resin of commerce.

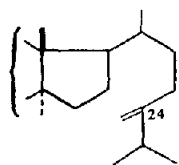
From balata resin, Tschirch<sup>1</sup> isolated balataresinol which he formulated as  $C_{27}H_{46}O_2$  or  $C_{27}H_{44}O_2$ , while Tanaka<sup>2</sup> isolated an alcohol, balatol, which was formulated as  $C_{32}H_{52}O_2$ . The similarity of balatol and balataresinol to resiniferol,  $C_{30}H_{50}O$ , isolated from *Euphorbia resinifera*, was observed by Julia,<sup>3</sup> who suggested that these materials were identical. Cocker<sup>4</sup>



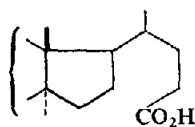
(Ia)  $R = H, R' = CH_3$   
(Ib)  $R = H, R' = H$



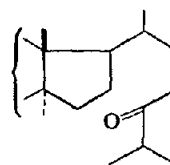
(IIa)  $R = H, R' = CH_3$   
(IIb)  $R = Bz, R' = CH_3$



(IIIa)  $R = H, R' = CH_3$   
(IIIb)  $R = Bz, R' = CH_3$



(IV)  $R = Ac, R' = CH_3$



(V)  $R = Ac, R' = CH_3$

isolated a similar alcohol from the heartwood of *M. globosa*, and showed that it was a mixture of cyclolaudenol (Ia) and an unidentified alcohol, which was later characterized by Ourisson<sup>5</sup> as the  $C_4$ -monomethyl analogue (Ib) of cyclolaudenol.

<sup>1</sup> A. TSCHIRCH and O. MULLER, *Arch. Pharm.* **243**, 114 (1905); A. TSCHIRCH and E. SCHERESCHEWSKI, *Arch. Pharm.* **243**, 358 (1905).

<sup>2</sup> Y. TANAKA, T. KUWATA and T. SUZUKI, *J. Soc. Chem. Ind. Japan* **38**, 504B (1935).

<sup>3</sup> G. DUPONT, M. JULIA and W. R. WRAGG, *Bull. Soc. Chim. F.* 852 (1953).

<sup>4</sup> W. COCKER and S. J. SHAW, *J. Chem. Soc.* 677 (1963).

<sup>5</sup> G. BERTI, F. BOTTARI, B. MACHIA, A. MARSIL, G. OURISSON and H. PIOTROWSKA, *Bull. Soc. Chim. F.* 2359 (1964).

Our examination of the non-saponifiable portion of balata resin did not reveal the presence of cyclolaudenol (Ia), but the related tetracyclic triterpenes, cycloartenol (IIa) and 24-methylenecycloartanol (IIIa) were identified along with squalene,  $\beta$ -amyrin and lupeol. The ketones derived from the above alcohols, viz. cycloartenone, 24-methylenecycloartanone,  $\beta$ -amyrenone and lupenone, were also identified as constituents of the resin. It is of interest to note that balata resin, besides affording a convenient source of all-*trans* squalene, contains triterpenoids which are derivable from squalene on current theories of biogenesis.<sup>6</sup>

## EXPERIMENTAL

Hydrolysis of the resin with ethanolic KOH (10%) and isolation of the product through ether afforded a non-saponifiable fraction (90% of resin) which was chromatographed on alumina. Elution with light petroleum afforded fraction A (16% of resin), while light petroleum-benzene (4:1) gave a mixture of ketones (fraction B). Final elution with Et<sub>2</sub>O-MeOH (19:1) afforded a mixture of alcohols (fraction C).

*Fraction A.* This was shown to be identical (i.r., NMR, mass spectra, GLC, thiourea adduct) with an authentic specimen of all-*trans* squalene.

*Fraction C.* The mixed alcohols (72 g) in pyridine (150 ml) containing benzoyl chloride (65 ml) were heated at 100° (15 hr) and the derived benzoates (110 g) were dissolved in acetone (250 ml) and kept at 0° (2 hr). The solid which separated, crop *a*, (9.5 g) was recrystallized from acetone and afforded lupenyl benzoate identical (m.p.,  $[\alpha]_D$ , i.r.) with an authentic sample. Identity was confirmed by conversion to lupeol and lupenyl acetate. After removal of lupenyl benzoate by filtration the original mother liquor was kept at 0° (30 min) when a second crop (*b*) was obtained which crystallized from acetone to give a mixture (GLC) (6.9 g), m.p. 117–119°  $[\alpha]_D + 70^\circ$ . The crop *b* mother liquors, on standing overnight at 0°, deposited a third crop (*c*) (12.5 g).

The crop *b* benzoates (2.2 g) were chromatographed on silica gel impregnated with AgNO<sub>3</sub>.<sup>7</sup> Elution with light petroleum-benzene (2:1) afforded cycloartenyl benzoate (IIb) (0.9 g), from acetone, m.p. 131°,  $[\alpha]_D + 75^\circ$  (lit.,<sup>8</sup> m.p. 130°,  $[\alpha]_D + 76^\circ$ ). The i.r. spectrum was superimposable on that of an authentic specimen. The identity of the benzoate (IIb) was further confirmed by its conversion to the known 3 $\beta$ -acetoxy trisnorcycloartanoic acid (IV).<sup>9</sup> Continued elution of the column with the same solvent afforded a mixture which was later followed by 24-methylenecycloartanyl benzoate (0.3 g) (IIIb) crystallized from acetone, m.p. 156–158°,  $[\alpha]_D + 59.5^\circ$  (lit.,<sup>9</sup> m.p. 156–157°;  $[\alpha]_D + 62^\circ$ ). The i.r. spectrum was identical with that of an authentic sample, while conversion of the benzoate to the known 24-oxo derivative (V)<sup>10</sup> confirmed its structure.

The crop *c* benzoates were recrystallized from ethyl acetate to give  $\beta$ -amyrin benzoate (m.p., mixed m.p. and  $[\alpha]_D$ ; m.p., mixed m.p. and  $[\alpha]_D$  of acetate, also i.r. identity).

*Fraction B.* This consisted of ketones (i.r.) which could not be separated by column chromatography. The constitution of the mixture was established by reduction of the mixture with LiAlH<sub>4</sub>, conversion of the derived alcohols to benzoates and proceeding as described under fraction C when the same benzoates were isolated.

*Acknowledgements*—The authors thank Telcon Plastics Ltd. for a generous gift of balata resin and the University of Ife for study leave (to O. O. O.).

<sup>6</sup> R. B. CLAYTON, *Quart. Rev.* **19**, 168 (1965); E. E. VAN TAMELEN, *Acc. Chem. Res.* **1**, 111 (1968).

<sup>7</sup> A. S. GUPTA and S. DEV, *J. Chromatog.* **12**, 189 (1963).

<sup>8</sup> D. H. R. BARTON, *J. Chem. Soc.* 1444 (1951).

<sup>9</sup> G. OHTA, *Chem. and Pharm. Bull. Japan* **8**, 9 (1960).

<sup>10</sup> G. OHTA and M. SHIMIZU, *Chem. and Pharm. Bull. Japan* **6**, 325 (1958).